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The Anomeric 2,3,5-Tri-*O*-benzoyl-D-arabinosyl Bromides and Other D-Arabinofuranose Derivatives

BY ROBERT K. NESS AND HEWITT G. FLETCHER, JR.

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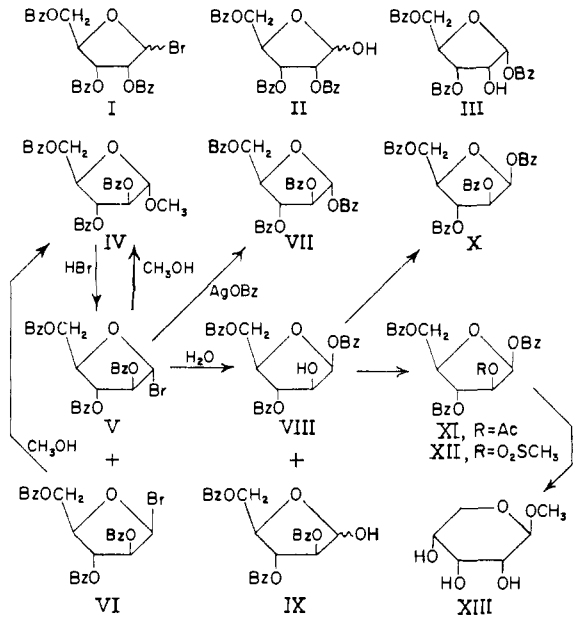
Methyl α-D-arabinofuranoside tribenzoate, prepared directly from D-arabinose, gives, on treatment with hydrogen bromide in glacial acetic acid, two new crystalline substances which are shown to be the anomeric halides, 2,3,5-tri-*O*-benzoyl-α-D-arabinosyl bromide (V) and 2,3,5-tri-*O*-benzoyl-β-D-arabinosyl bromide (VI). Both bromides react very rapidly with methanol, the β-anomer being observably slower than the α-anomer. Hydrolysis of the β-anomer gives only amorphous material; hydrolysis of the α-anomer gives amorphous material and a crystalline tri-*O*-benzoyl-D-arabinose. Benzoylation of the new tribenzoate gives β-D-arabinofuranose tetrabenzoate (X); treatment of the α-bromide with silver benzoate gives the anomeric α-D-arabinofuranose tetrabenzoate. The new tribenzoate is stable in anhydrous pyridine but mutarotates slightly in aqueous pyridine giving an amorphous product. Alkaline methanolysis of the methylsulfonyl ester of the new tribenzoate led to the isolation of methyl β-D-ribopyranoside (XIII) as its tribenzoate. This evidence is regarded as establishing structure VIII, 1,3,5-tri-*O*-benzoyl-β-D-arabinose. It is evident, then, that the C2 benzoyl group in the *trans*-halide V has migrated to C1 during the hydrolysis.

Recent researches in this Laboratory have shown[1-3] that the hydrolysis of amorphous 2,3,5-tri-*O*-benzoyl-D-ribosyl bromide (I) under neutral or acidic conditions affords two crystalline D-ribofuranose tribenzoates: 2,3,5-tri-*O*-benzoyl-D-ribose (II), which may be regarded as the normal product of the reaction and 1,3,5-tri-*O*-benzoyl-α-D-ribose (III), a structure arising through the shifting of a benzoyl group from C2 to C1. While this type of acyl migration, accompanying the hydrolysis of an aldosyl halide, may have been encountered earlier (as, for instance, in the celtrobiose series[1,4]), acyl



migrations in aldose derivatives are normally catalyzed by alkali and proceed in a direction away from the reducing carbon. Partly for this reason, the new type of acyl migration seemed worthy of further study.

In view of the well-recognized participation of neighboring acyl groups in halogen displacements, it seems likely that only the *trans*-isomer, 2,3,5-tri-*O*-benzoyl-β-D-ribosyl bromide, undergoes acyl migration on hydrolysis; barring participation of the benzoyloxy group at C5,[5] the *cis*-isomer, 2,3,5-tri-*O*-benzoyl-α-D-ribosyl bromide, should undergo hydrolysis without rearrangement. Unfortunately the halide I has not, as yet, been obtained in crystalline form and so its anomeric nature remains uncertain. We have turned our attention, therefore, to the D-arabinofuranose series in the hope of obtaining two anomeric tri-*O*-benzoyl-D-arabinofuranosyl halides for individual study. This work will now be described.

When D-arabinose was treated with methanol containing *ca.* 1% of hydrogen chloride and the reaction halted as soon as the reducing power of the sugar had disappeared, a sirupy product was obtained which periodate oxidation showed to be largely methyl D-arabinofuranoside. Benzoylation led to the isolation of a crystalline methyl D-arabinofuranoside tribenzoate of m.p. 101–103° and $[\alpha]^{20}D$ −19.5° ($CHCl_3$) in 50% yield. With hydrogen bromide in glacial acetic acid this glycoside lost its alkoxyl group and afforded two crystalline tri-*O*-benzoyl-D-arabinosyl bromides which rotated $[\alpha]^{20}D$ +84.8° (CH_2Cl_2) and $[\alpha]^{20}D$ −138° (CH_2Cl_2). On solvolysis with methanol in the absence of an acid acceptor both halides gave the original methyl D-arabinofuranoside tribenzoate in high yield, the final rotations of the reaction mixtures indicating that little, if any, by-product was formed. Since such solvolyses have always been found to lead to *trans* products, we may conclude with considerable certainty (a) that the halides represent an anomeric pair (V and VI) and (b) that the glycoside is methyl α-D-arabinofuranoside tribenzoate (IV). On the basis of rotatory power the dextrorotatory bromide is presumed to be the α-anomer V and its levorotatory isomer the β-anomer VI. Thus, for the first time, as far as we are aware, an anomeric pair of crystalline furanosyl halides is now readily accessible. Two anomeric pairs of tri-*O*-benzoyl-D-ribopyranosyl halides have previously been reported by us.[6]

(1) R. K. Ness and H. G. Fletcher, Jr., THIS JOURNAL, **78**, 4710 (1956).

(2) R. K. Ness and H. G. Fletcher, Jr., *ibid.*, **76**, 1663 (1954).

(3) R. K. Ness, H. W. Diehl and H. G. Fletcher, Jr., *ibid.*, **76**, 763 (1954).

(4) N. K. Richtmyer and C. S. Hudson, *ibid.*, **58**, 2534 (1936).

(5) *Cf.* R. K. Ness and H. G. Fletcher, Jr., *J. Org. Chem.*, **22**, 1465 (1957), where this matter is discussed briefly in connection with reactions of 3,5-di-*O*-benzoyl-D-ribosyl chloride.

(6) R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **73**, 959 (1951).

While, as pointed out earlier, 2,3,5-tri-*O*-benzoyl-D-ribosyl bromide is of limited use for stereochemical studies because of its amorphous character[7] the two new 2,3,5-tri-*O*-benzoyl-D-arabinosyl bromides offer a number of interesting opportunities for investigating reaction mechanisms. If the assignments of anomeric configuration are correct one may, for instance, predict that, owing to the participation of the benzoyloxy group at C2, the solvolysis of the α-(*trans*)-isomer will be more rapid than that of the β-(*cis*)-isomer. This was actually shown in a qualitative fashion, the methanolysis of the α-anomer being too rapid to detect and that of the β-anomer being too rapid for accurate measurement. The rapidity of these reactions may be considered as normal for aldofuranosyl halides; the methanolysis of the corresponding ribopyranosyl halides had been studied earlier[6] and found to be sufficiently slow for kinetic measurements.

We wish especially to draw attention to the fact that the formation of polyacylglycosyl halides is thermodynamically controlled while the solvolysis of such halides is kinetically controlled. Failure to understand this matter has resulted in the widely held misconception that the only halide isolated in a given series, or that which is formed in greater quantity, is of necessity the more stable isomer in solvolytic reactions.

With a pair of crystalline, anomeric furanosyl halides in hand we turned our attention to hydrolysis and the concomitant problem of acyl migration. If our view of the mode of formation of II and III, as described earlier, is correct, we may predict that the *trans*-halide 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl bromide (V) would, on hydrolysis, afford both 2,3,5-tri-*O*-benzoyl-D-arabinose (IX) and 1,3,5-tri-*O*-benzoyl-D-arabinose (VIII) while the *cis*-bromide VI would give only the former compound IX. Experiment showed this to be true: the *trans*-bromide gave a crystalline D-arabinose tribenzoate together with considerable amorphous material while the *cis*-bromide gave only amorphous material. The presumption that the crystalline product was 1,3,5-tri-*O*-benzoyl-β-D-arabinose (VIII, arising through wandering of the benzoyl group at C2 in the halide) was justified by several methods.[8] As might be expected of an aldose substituted at C1, the new D-arabinofuranose tribenzoate failed to mutarotate in neutral solution or in anhydrous pyridine. However, in aqueous pyridine its rotation changed slightly and no crystalline product could be isolated after removal of the solvent. In view of the great ease with which a 1-acyl group migrates to a *cis*-C2 position[9] this behavior is in agreement with structure VIII. In order to undergo such a C1 to C2 migration under alkaline conditions the D-arabinofuranose tribenzoate would, of necessity, have to be the β-anomer. Benzoylation in anhydrous pyridine would convert it into β-D-arabinofuranose tetrabenzoate (X). This, too, was found to be the case, a crystalline D-arabinofuranose tetrabenzoate of $[\alpha]^{20}D$ −95.2° ($CHCl_3$) being isolated in 66% yield after benzoylation of the crystalline tribenzoate. Treatment of 2,3,5-tri-*O*-benzoyl-α-D-arabinosyl bromide with silver benzoate (a reaction generally recognized as affording only *trans*-isomers[10]) gave a second crystalline D-arabinofuranose tetrabenzoate showing $[\alpha]^{20}D$ +27.9° ($CHCl_3$). The molecular rotations of these two new pentofuranose tetrabenzoates, doubtless anomers, may be compared with those of similar pairs in the D-ribose and D-xylose series in Table I.

TABLE I

Tetrabenzoate	$[\alpha]^{20}D$ ($CHCl_3$)	$[M]^{20}D$	Difference (2A)
α-D-Arabinofuranose	+27.9°	+15,800	69,700
β-D-Arabinofuranose	−95.2°	−53,900	
α-D-Xylofuranose	+170°[a]	+96,300	89,940
β-D-Xylofuranose	+11.4°[a]	+ 6,460	
α-D-Ribofuranose	+90.4°[b]	+51,200	41,570
β-D-Ribofuranose	+17.0°[c]	+ 9,630	

[a] H. G. Fletcher, Jr., THIS JOURNAL, **75**, 2624 (1953). [b] Amorphous but chromatographically homogeneous: ref. 1. [c] Ref. 3.

In earlier work[1] the structure of 1,3,5-tri-*O*-benzoyl-α-D-ribose (III) was ascertained through treatment of its 2-*O*-methylsulfonyl derivative with sodium methoxide, the methyl α-D-arabinopyranoside formed demonstrating that the free hydroxyl group in the tribenzoate had been at C2. The same process was now applied to the new D-arabinofuranose tribenzoate, its crystalline *O*-methylsulfonyl derivative XII being treated with an excess of sodium methoxide. The product proved to be a mixture, chromatography revealing two components migrating at the same rates as methyl β-D-ribofuranoside and methyl β-D-ribopyranoside (XIII). Hydrolysis of a sample of the mixed glycosides, followed by chromatography, showed ribose, a trace of arabinose and two other minor, unidentified components. Benzoylation of the mixture of methyl glycosides led, after chromatography, to the isolation of the known methyl β-D-ribopyranoside tribenzoate. The formation of a ribose derivative here conclusively locates the free hydroxyl group in the D-arabinofuranose tribenzoate as at C2 and structure VIII may then be assigned to the substance.

The mechanism of the action of sodium methoxide on 1,3,5-tri-*O*-benzoyl-2-*O*-methylsulfonyl-α-D-ribose previously has been discussed by us.[1] D. C. C. Smith[11] has recently investigated the action of sodium methoxide on the pyranose derivative 4-*O*-formyl-2-*O*-methylsulfonyl-D-arabinose. Methyl β-D-ribopyranoside was isolated and evidence obtained which indicated the formation of both of the anomeric methyl D-arabinofuranosides.

In connection with the C1 to C2 acyl migrations mentioned here and in earlier papers it is of interest to note that C. L. Stevens and his associates[12]

(7) While the anomeric ratio of this bromide is not known, its reactions tend to suggest that at least a substantial quantity of the β-anomer is present.

(8) It seems likely that the amorphous material, which was not investigated further, is largely 2,3,5-tri-*O*-benzoyl-D-arabinose although the presence of 1,2,3-tri-*O*-benzoyl-β-D-arabinose, arising from migration of the benzoyl group at C5 in the α-halide, is not excluded.

(9) H. B. Wood, Jr., and H. G. Fletcher, Jr., THIS JOURNAL, **78**, 2849 (1956).

(10) *Cf.* H. B. Wood, Jr., and H. G. Fletcher, Jr., *ibid.*, **79**, 3234 (1957).

(11) D. C. C. Smith, *J. Chem. Soc.*, 2690 (1957).

(12) C. L. Stevens and B. T. Gillis, THIS JOURNAL, **79**, 3448 (1957), and earlier papers of this series.

have shown that α-hydroxyacylals readily undergo acyl migration to give esters of α-hydroxyaldehydes or ketones.

While the work described here was in progress Drs. R. S. Wright and H. G. Khorana[13] independently made methyl α-D-arabinofuranoside tribenzoate by a method very similar to ours. The constants found by the Vancouver workers are close to ours and are quoted in the experimental part for comparison purposes.

Acknowledgments.—We are indebted to Mr. Harry W. Diehl for assistance in certain of the preparations and to the Institutes' Microanalytical Laboratory for elementary analyses carried out under the direction of Dr. W. C. Alford.

Experimental[14]

Methyl α-D-Arabinofuranoside Tribenzoate (IV) from D-Arabinose.—A mixture of 10.0 g. of D-arabinose, 200 ml. of absolute methanol and 63 ml. of 1.06 *N* methanolic hydrogen chloride was stirred at room temperature until solution was complete. After 3.78 hr. the solution no longer reduced Fehling solution and was immediately treated with 37 ml. of dry pyridine. Solvent was removed *in vacuo* and the residual sirup diluted with 30 ml. of dry pyridine which was then evaporated *in vacuo* (70° bath) in order to remove the last traces of methanol. Benzoylation of the residue with benzoyl chloride (31 ml.) in pyridine (75 ml.) was conducted in the usual manner, the reaction mixture being heated eventually at 55° for 25 min. before the excess of benzoyl chloride was destroyed by the addition of a small amount of water. Methylene chloride was added and the solution washed successively with water, 3 *N* sulfuric acid and saturated aqueous sodium bicarbonate. Moisture was removed with sodium sulfate and the solution concentrated *in vacuo* to give a sirup which, from 50 ml. of absolute ethanol, afforded 15.7 g. (50%) of crystalline product, m.p. 100–102°. The material in the mother liquor gave from ether–pentane a second crop (0.98 g., 3.1%) of almost equally pure material. Two recrystallizations from absolute ethanol afforded methyl α-D-arabinofuranoside tribenzoate melting at 101–103° and rotating $[\alpha]^{20}D$ −19.5° in chloroform (*c* 2.67).

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08. Found: C, 67.85; H, 5.26.

Wright and Khorana[13] found m.p. 100–101.5° and $[\alpha]^{21}D$ −19.1° ($CHCl_3$, *c* 2.05) for this substance.

In one experiment, D-arabinose was treated with methanolic hydrogen chloride as described above and, when the solution was no longer reducing, the acid was removed with silver carbonate. The solvent-free sirup obtained therefrom was found to consume 1.21 moles of sodium metaperiodate and liberate 0.17 mole of formic acid in the course of 18 hr. After 45 hr. these values were 1.23 and 0.22, respectively; a mixture of 23% of pentopyranoside and 77% of pentofuranoside would be expected to reduce 1.23 moles of periodate and to furnish 0.23 mole of formic acid.

The Anomeric 2,3,5-Tri-O-benzoyl-D-arabinosyl Bromides (V and VI).—To a solution of 10.0 g. of methyl α-D-arabinofuranoside tribenzoate in 50 ml. of glacial acetic acid was added 50 ml. of 32% (w./w.) hydrogen bromide–glacial acetic acid. After 20 min. at room temperature the solution was diluted with 300 ml. of methylene chloride and poured into *ca.* 1 l. of ice-water. The organic layer was quickly washed with sodium bicarbonate solution, dried with sodium sulfate and concentrated *in vacuo* (45° bath). The sirup thus obtained was dissolved in 50 ml. of absolute ether to give, after 4 hr. at room temperature, 4.2 g. of crystalline product melting at 103–105°. Recrystallization at room temperature from 75 ml. of 2:1 ether–pentane gave 4.0 g. of pure **2,3,5-tri-O-benzoyl-α-D-arabinosyl bromide (V)** as prisms melting at 103–104° and rotating $[\alpha]^{20}D$ +84.8° in dry methylene chloride (*c* 1.15, no mutarotation observed after 2 hr.).

Anal. Calcd. for $C_{26}H_{21}O_7Br$: C, 59.44; H, 4.03; Br, 15.21. Found: C, 59.64; H, 4.22; Br, 15.43.

The addition of 35 ml. of pentane to the mother liquor (from which the first crop of the α-anomer had just been removed) gave, after 2 hr., 2.5 g. more α-anomer (m.p. 102–103°). Chilling the filtrate to −5° then afforded 1.6 g. of fine needles melting at 94–98°. Recrystallized from 15 ml. of ether, the product (0.24 g.) melted at 129–130°; a second recrystallization from ether gave pure **2,3,5-tri-O-benzoyl-β-D-arabinosyl bromide (VI)** melting at 130–132° and rotating $[\alpha]^{20}D$ −138° in dry methylene chloride (*c* 0.88).

Anal. Calcd. for $C_{26}H_{21}O_7Br$: C, 59.44; H, 4.03. Found: C, 59.58; H, 4.24.

Methyl α-D-Arabinofuranoside Tribenzoate (IV). (a) **From 2,3,5-Tri-O-benzoyl-α-D-arabinosyl Bromide (V).**—The α-bromide (0.2278 g.) was dissolved in 2.5 ml. of pure dioxane and 35 sec. later the solution was diluted to 25.0 ml. with absolute methanol. Observed in a 1.5-dm. tube at 20°, the solution showed an observed rotation of −0.14° (1.25 min., unchanged after 20 min.). On the assumption that complete conversion to methyl pentoside tribenzoate had taken place, this rotation corresponds to $[\alpha]^{20}D$ −11°. Methyl α-D-arabinofuranoside tribenzoate shows $[\alpha]^{20}D$ −10.1° in 1:9 dioxane–methanol (v./v) (*c* 1.09). After 25 min. the reaction mixture was concentrated *in vacuo* to a sirup. Ether was evaporated from the sirup which was then dissolved in ether–pentane to give 0.1750 g. (85%) of crystalline product melting at 101–103°. A mixed melting point with methyl α-D-arabinofuranoside tribenzoate, prepared from D-arabinose as described earlier, was undepressed.

(b) **From 2,3,5-Tri-O-benzoyl-β-D-arabinosyl Bromide (VI).**—The β-bromide (0.0294 g.) was dissolved in 1.0 ml. of purified dioxane and the resulting solution diluted to 10.0 ml. with absolute methanol. In a 1.5-dm. tube at 20° the following rotations were observed: −0.24° (1.3 min.), −0.15° (2 min.), −0.09° (2.8 min.), −0.06° (3.7 min.) and −0.05° (5.2, 20 and 60 min.). Based on the assumption that complete conversion to methyl pentoside tribenzoate had taken place, the final rotation corresponds to $[\alpha]^{20}D$ −12°; as stated above, methyl α-D-arabinofuranoside tribenzoate shows $[\alpha]^{20}D$ −10.1° in this solvent mixture. After 1 hr. the reaction mixture was concentrated *in vacuo* to a sirup from which a small amount of toluene and ether were successively evaporated. From ether–pentane the residue afforded 21.8 mg. (82%) of crystalline material melting at 101–103° either alone or in admixture with methyl α-D-arabinofuranoside tribenzoate prepared from D-arabinose as described earlier.

α-D-Arabinofuranose Tetrabenzoate (VII) from 2,3,5-Tri-O-benzoyl-α-D-arabinosyl Bromide (V).—One gram of 2,3,5-tri-O-benzoyl-α-D-arabinosyl bromide was added to a rapidly stirred suspension of 1.7 g. of silver benzoate in 15 ml. of dry benzene. After 8 min. the silver salts were removed by filtration and washed with methylene chloride. Concentration *in vacuo* of the combined filtrate and washings gave a sirup which from ether–pentane afforded 0.88 g. (82%) of clear prisms melting at 117–121°. The product was dissolved in methylene chloride and brought to crystallization by concentration and addition of ether. A second recrystallization from ethanol yielded pure α-D-arabinofuranose tetrabenzoate melting at 117–121° and rotating $[\alpha]^{20}D$ +27.9° in chloroform (*c* 2.13).

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.96; H, 4.63. Found: C, 69.83; H, 4.79.

Hydrolysis of 2,3,5-Tri-O-benzoyl-α-D-arabinofuranosyl Bromide (V). 1,3,5-Tri-O-benzoyl-β-D-arabinose (VIII).—The α-bromide (1.00 g.) was dissolved in 10 ml. of 1:9 (v./v.) water–acetone and observed polarimetrically at 20° in a 1.5-dm. tube: $\alpha^{20}D$ −1.75° (2.5 and 20 min.). After 20 min. the reaction mixture was concentrated *in vacuo* to a mixture of sirup and water. Ether was added and the water separated. Removal of ether gave a sirup which, from ether–pentane, afforded 0.19 g. (22%) of crystalline material melting at 119–121°. Recrystallization from ether–pentane gave pure 1,3,5-tri-O-benzoyl-β-D-arabinose melting at 120–121° and rotating $[\alpha]^{20}D$ −9.7° in chloroform (*c* 1.00). In aqueous dioxane the rotation of the tribenzoate was constant over a period of 12 min. A sample (74.0 mg.) in 5.0 ml. of dry pyridine likewise showed no mutarotation in 30 min. (1.5-dm. tube, $\alpha^{20}D$ −0.64°); when 1.0 ml. of water was added the following rotations (1.5-dm. tube)

(13) R. S. Wright and H. G. Khorana, THIS JOURNAL, **80**, 1994 (1958).

(14) Melting points are corrected.

were observed: −0.54° (1.3 min., 45 min.), and −0.60° (200 and 400 min.). Attempts to recover crystalline material from the solution after 7 hr. were unsuccessful.

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.52; H, 4.80. Found: C, 67.29; H, 4.97.

In another, larger-scale hydrolysis (which gave the same product in 27% yield) the material remaining in the mother liquor was treated with a mixture of acetic anhydride, acetic acid and hydrogen bromide. Subsequent hydrolysis afforded a second batch of 1,3,5-tri-*O*-benzoyl-β-D-arabinose and raised the total yield of this product to 39%.

β-D-Arabinofuranose Tetrabenzoate (X) from 1,3,5-Tri-*O*-benzoyl-β-D-arabinose (VIII).—A cold mixture of 1.0 ml. of dry pyridine and 0.20 ml. of benzoyl chloride was added to 68.1 mg. of 1,3,5-tri-*O*-benzoyl-β-D-arabinose. After 15 min. at 0° the reaction mixture was held at room temperature for one hour before the excess of benzoyl chloride was destroyed through the addition of a drop of water. Ten minutes later, much water was added, the product precipitating as a crystalline mass which was recrystallized from absolute ethanol: 55 mg. (66%), m.p. 120–122°, $[\alpha]^{20}D$ −94.0° ($CHCl_3$, *c* 2.19). One further recrystallization from ethanol gave pure β-D-arabinofuranose tetrabenzoate melting at 121–122° and showing $[\alpha]^{20}D$ −95.2° in chloroform (*c* 1.86).

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.96; H, 4.63. Found: C, 70.12; H, 4.51.

2-*O*-Acetyl-1,3,5-tri-*O*-benzoyl-β-D-arabinose (XI).—A cold mixture of 1.0 ml. of dry pyridine and 0.20 ml. of acetic anhydride was added to 101.8 mg. of 1,3,5-tri-*O*-benzoyl-β-D-arabinose. After 45 min. at 0° and 17 hr. at room temperature excess of acetic anhydride was decomposed by the addition of water. The crystalline product thus obtained was washed with water, dried and recrystallized from 8 ml. of 1:1 absolute ethanol–pentane: 99.5 mg. (90%), m.p. 132–134°. Further recrystallization of the fine needles from ether did not raise this melting point. The pure 2-*O*-acetyl-1,3,5-tri-*O*-benzoyl-β-D-arabinose rotated $[\alpha]^{20}D$ −60.4° in chloroform (*c* 1.91).

Anal. Calcd. for $C_{28}H_{24}O_9$: C, 66.66; H, 4.80. Found: C, 66.86; H, 4.84.

1,3,5-Tri-*O*-benzoyl-2-*O*-methylsulfonyl-β-D-arabinose (XII).—Crystalline 1,3,5-tri-*O*-benzoyl-β-D-arabinose (2.00 g.) was added portionwise over a period of 2 min. to a cold mixture of 4 ml. of dry pyridine and 0.4 ml. of methanesulfonyl chloride. After 1.2 hr. at room temperature the reaction mixture was diluted with methylene chloride and washed successively with 3 *N* sulfuric acid and saturated aqueous sodium bicarbonate. The solution was dried with sodium sulfate and concentrated *in vacuo* to a crystalline mass. Recrystallized from methylene chloride–ethanol the product (2.29 g., 98%) melted at 154–155° after sintering at 148°. One further recrystallization from ethyl acetate gave the pure ester showing a double melting point, 147°; 154–156° and rotating $[\alpha]^{20}D$ −41.0° in chloroform (*c* 1.28).

Anal. Calcd. for $C_{27}H_{24}O_{10}S$: C, 59.99; H, 4.48; S, 5.93. Found: C, 59.71; H, 4.48; S, 5.91.

Treatment of 1,3,5-Tri-*O*-benzoyl-2-*O*-methylsulfonyl-β-D-arabinose (XII) with Sodium Methoxide.—To a suspension of the ester (1.80 g., 0.00333 mole) in 20 ml. of absolute methanol was added slowly 2.2 ml. of 1.3 *N* sodium methoxide. After 10 min. solution was complete and 1 ml. more of the sodium methoxide solution was added. Sodium methanesulfonate was observed to precipitate. A further 3.8 ml. of the sodium methoxide solution (to make a total of 0.009 mole) was added and the reaction mixture left at room temperature overnight. Two drops of water were added and carbon dioxide then passed in until the mixture was neutral. After removal of the precipitate the solution was concentrated *in vacuo* to a sirup which was dissolved in 30 ml. of water and extracted with methylene chloride to remove methyl benzoate. It was then passed successively through Amberlite IR-100 and Duolite A-4 to give a neutral solution which was concentrated *in vacuo* (60° bath) to a sirup. The mixture was then dissolved in ethanol, the solution clarified by filtration through Super-Cel and reconcentrated to a sirup (0.47 g.) which reduced Fehling solution. Ascending paper partition chromatography of a sample on Whatman #1 paper using 2-butanone saturated with water and Lemieux and Bauer's[15] $NaIO_4$–$KMnO_4$ spray reagent revealed five components which, relative to methyl β-D-ribopyranoside, had the following migration rates (averages from two determinations): 1.00, 0.83, 0.22, 0.09, 0.00. Simultaneous chromatography under identical conditions with known substances gave the following values: D-ribose, 0.20; D-arabinose, 0.08; D-lyxose, 0.12; methyl α-D-arabinopyranoside, 0.26; methyl α-D-arabinofuranoside, 0.94; methyl β-D-ribopyranoside, 1.00; methyl β-D-ribofuranoside, 0.84. Attempts to crystallize the sirup failed. A sample (10.03 g.) was dissolved in 2.5 ml. of *N* hydrochloric acid and heated on the steam-bath for 1.7 hr. Descending paper partition chromatography of the product in 3:2:1.5 1-butanol–pyridine–water revealed components with the following migration rates relative to ribose: 1.01, 0.74, 0.11, 0.00. Under the same conditions known substances gave values as follows: D-ribose, 1.00; D-arabinose, 0.73; D-lyxose, 0.94; D-xylose, 0.90. In the chromatogram of the reaction mixture the spot corresponding to D-arabinose was relatively weak compared with that corresponding to D-ribose.

A portion (0.43 g.) of the sirup was extracted with hot ethyl acetate and the extract concentrated to a sirup (0.38 g.) which was benzoylated in the usual manner using 3 ml. of dry pyridine and 1.0 ml. of benzoyl chloride. After the customary removal of reagents the resulting oil (1.12 g.) was chromatographed on alumina to give from ether–pentane 131.4 mg. of crystalline product which rotated $[\alpha]^{20}D$ −70.7° ($CHCl_3$, *c* 2.02) and melted at 109–110° either alone or in admixture with authentic methyl β-D-ribopyranoside tribenzoate. The pure ester has been recorded[16] as melting at 109–110° and rotating −69.5° ($CHCl_3$, *c* 0.82).

(15) R. U. Lemieux and H. F. Bauer, *Anal. Chem.*, **26**, 920 (1954).

(16) R. W. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **70**, 4055 (1948).

BETHESDA, MD.

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, THE DOW CHEMICAL COMPANY]

Studies on the Enzyme Dextransucrase. I. The Effect of *p*H on Enzyme Activity

BY W. BROCK NEELY

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The Michaelis constant and maximum initial velocity for the enzymatic formation of dextran fron sucrose were determined at various hydrogen ion concentrations. A mechanism is postulated for the above results. The scheme that is presented indicates a bifunctional catalytic role for the enzyme. The *pK* values of the active sites correspond to a carboxyl and an imidazole group.

In 1941–42 it was first demonstrated that cell free extracts of *Leuconostoc mesenteroides* were found to bring about the formation of dextran from sucrose.[1,2] By the action of the enzyme, sucrose is converted to dextran and one molecular equivalent of fructose.[1,2] The over-all reaction is represented in equation 1

$$n\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + \underset{\text{acceptor}}{HOR} \longrightarrow \underset{\text{dextran}}{H(C_6H_{10}O_5)_nOR} + \underset{\text{fructose}}{nC_6H_{12}O_6} \quad (1)$$

(1) E. J. Hehre, *Science*, **93**, 237 (1941).

(2) E. J. Hehre and J. Y. Sugg, *J. Exptl. Med.*, **75**, 339 (1942).